Standard Operating Procedure for Nitrate, Nitrite (Lachat Method)

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April 5, 1995

Revision 2

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1.0 Scope and Application

1.1 This method covers the determination of nitrate and nitrite in lake/rain water.

1.2 The approximate working range is 0.03 to 2.00 mg N(as NO_3 + NO_2)/L. The method detection limit is 0.03 mg N/L.

2.0 Summary

Nitrate is quantitatively reduced to nitrite by passage of the sample through a column containing copper coated cadmium. The nitrate (reduced nitrate plus original nitrite) is determined by diazotizing with sulfanilamide dihydrochloride. The resulting water soluble dye has a magenta color which is read at 520 nm.

3.0 Sample Handling and Preservation

3.1 Samples are collected in clean glass or plastic containers. Flexidome and phenolic resin (black) caps, or caps with glued plastic liners may contaminate the samples. Polypropylene caps should be used.

3.2 Samples are preserved by addition of 1 mL of concentrated sulfuric acid per liter of sample.

4.0 Interferences

4.1 Residual chlorine can interfere by oxidizing the cadmium column.

4.2 Low results would be obtained for samples that contain high concentrations of iron, copper, or other metals. In this method, EDTA is added to the buffer to reduce this interference.

5.0 Apparatus

5.1 13 x 100 mm test tubes

5.2 Lachat QuikChem AE

5.2.1 XYZ Sampler

5.2.2 Nitrate/Nitrite Manifold (Lachat Method # 10-107-04-1-C)

5.2.3 Cadmium-Copper Reduction Column

5.2.4 Printer

6.0 Reagents and Standards

6.1 All reagents should be stored in the appropriate bottles and labeled with the following information:

Identity:	(15 N Sodium hydroxide)
Date:	(mm/dd/yy)
Initials of Preparer:	(M.S.)

All standards will be stored in appropriate bottles and labeled as above with the following also included:

Concentration:	(1000 mg- N/L)

6.2 Use deionized water for all solutions.

6.3 15 N Sodium hydroxide: Add 150 g of NaOH very slowly to 250 mL of water.
Caution: The solution will get very hot! Swirl until dissolved. Cool and store in a plastic bottle.

6.4 Ammonium chloride buffer, pH 8.5: In a 1 L volumetric flask, dissolve 85.0 g ammonium chloride (NH_4Cl) and 1.0 g disodium ethylenediamine tetraacetic acid dihydrate ($Na_2EDTA \cdot 2H_20$) in about 800 mL water. Adjust pH to 8.5 with 15 N NaOH. Degas with helium.

6.5 Sulfanilamide color reagent: To a 1 L volumetric flask add about 600 mL water. Then add 100 mL of 85% phosphoric acid (H_3PO_4) 40.0 g sulfanilamide, and 1.0 g N-(1-naphthyl) ethylenediamine dihydrochloride (NED). Shake to wet, and stir to dissolve for 30 min. Dilute to the mark, and invert to mix. Store in a dark bottle. This solution is stable for one month. Degas with helium.

6.6 Preparation of Standards

6.6.1 Stock 1000 mg-N/L Nitrate Solution: Dissolve 7.218 g of potassium nitrate (KNO_3), dried for one hour at 105°C, in 500 mL of DI water. Add 1 mL of concentrated sulfuric acid (H_2SO_4) and dilute to 1 L.

6.6.2 Intermediate 100 mg-N/L Nitrate Standard Solution (Spike): Dilute 100 mL of stock nitrate solution (6.6.1) to 500 mL. Add 1 mL of concentrated sulfuric acid and dilute to 1 L with DI water. This solution is also the spike solution.

6.6.3 Working Standards: Prepare standards over the range of analysis. For the working range of 0-2.00 mg $N0_3$-N/L, the following standards may be used:

mL Intermediate Standard Solution (6.6.2) diluted to 1 L	Concentration mg-N/L
0.0	0.00
0.2	0.02
2.5	0.25
5.0	0.50
7.5	0.75
10.0	1.00
20.0	2.00

Note: Use volumetric flasks. Preserve the working standards by addition of 1 mL of concentrated sulfuric acid.

6.6.4 Stock 100 mg-N/L Nitrate Control Standards: Any nitrate compound may be used for control standards. They should be prepared by someone other than the analyst. Weigh 0.6068146 g of sodium nitrate ($NaNO_3$) (dried at 105°C for one hour) and dissolve in 500 mL of DI water. Add 1 mL concentrated H_2SO_4. Dilute to 1 L in volumetric flask with DI water.

6.6.5 Prepare the control standards using solution (6.6.4).

	mL Control Standard Solution (6.7.4) diluted to 1 L	Concentration mg-N/L
CS-1(LPC1)	6	0.600
CS-2(LPC-2)	2	0.200

Note: Use volumetric flasks. Preserve the control standards by addition of 1 mL of concentrated sulfuric acid.

7.0 Procedure

Follow the Lachat Procedural SOP (Typical Daily Operation Section). Remember to establish reagent flow through entire system before diverting flow through cadmium column.

8.0 Calculations

The computer yields results directly in mg-N(as NO_2+NO_3)/L.

9.0 Quality Control

The following items are required with the minimum frequency indicated.

	Audit	Type	Frequency	Limits
Rain:				
	CS-1(LPC-1)	Method	Beg, End, 1/40 Samp	0.60 ± 0.09
	CS-2(LPC-2)	Method	Beg, End, 1/40 Samp	0.20 ± 0.03
	Reagent Blank(LCB)	Method	Beg, End, 1/40 Samp	0.00 ± 0.03
	Lab. Blank(LRB)	Method	Beg, End, 1/40 Samp	0.00 ± 0.03
	Duplicate(LD)	Method	1/40 Samp	$\Delta \leq 0.03$
	Spike(LCO)	Method	1/40 Samp	100 ± 12%
Lake:				
	CS-1(LPC-1)	Method	Beg + End, 1/40 Samp	0.60 ± 0.09
	CS-2(LPC-2)	Method	Beg + End, 1/40 Samp	0.20 ± 0.03
	Reagent Blank(LCB)	Method	Beg + End, 1/40 Samp	0.00 ± 0.03

10.0 Waste Disposal

Effluent from this channel should be neutralized with sodium hydroxide to a pH of 6-9 and then washed down the laboratory drain with plenty of water.

11.0 Preventive Maintenance

Required maintenance is described in the Lachat Procedural SOP.

12.0 Troubleshooting

The most common problem is deactivation of the cadmium column which results in low values and non-linear calibration curves. The deactivation of the column is quantified by a column having a $\leq$89% efficiency factor. The only solution is replacement of the column. This procedure is outlined in the following section.

13.0 Cadmium Column Preparation

Note: Prepacked cadmium columns are available from Lachat Instruments.

13.1 Preparation of Reagents for Cadmium Column

13.1.1 1 N Hydrochloric acid (HCl): In a 100 mL container, add 8 mL concentrated HCl to 92 mL water. Stir to mix.

13.1.2 2% Copper Sulfate Solution: In a 1 L volumetric flask dissolve 20 g copper sulfate ($CuSO_4 \cdot 5H_20$) in about 800 mL water. Dilute to mark with water. Invert to mix thoroughly.

13.2 Cadmium Preparation

Place 10-20 g of coarse cadmium granules (0.3-1.5 mm diameter) in a 250 mL beaker. Wash with 50 mL of acetone, then water, then two 50 mL portions of 1 N HCl. Rinse several times with water.

13.3 Copperization

Add a 100 mL portion of 2% Copper Sulfate Solution to the cadmium prepared above. Swirl for about five minutes, then decant the liquid and repeat with a fresh 100 mL portion of the 2% copper sulfate solution. Continue this process until the blue aqueous copper color persist. Decant and wash with at least five portions of ammonium chloride buffer to remove colloidal copper. The cadmium should be black or dark gray. The copperized cadmium granule may be stored in a stoppered bottle under ammonium chloride buffer.

13.4 Packing the Column

Wear gloves and do all cadmium transfers over a special tray or beaker. Clamp the empty column upright so that your hands are free. Unscrew one of the colored fittings from an end of the column, and pull out and save the foam plug. The column and threads are glass so be careful not to break or chip them. Fasten this fitting up higher than the open end of the column and completely fill the column, attached fittings, and tubing with ammonium chloride buffer. Scoop up prepared copperized cadmium granules with a spatula and pour them unto the top of the filled column so that they sink down to the bottom of the column. Continue pouring the cadmium in and tapping the column with a screw driver handle to dislodge andy air bubbles and to prevent gaps in the cadmium filling. When the cadmium granules reach to about 5 mm form the open end of the column, push in the foam plug and screw on the top fitting. Rinse the outside of the column with DI water.

If air remains in the column or is introduced accidentally, connect the column into the manifold, turn the pump on maximum, and tap firmly with a screwdriver handle, working up the column until all air is removed.

13.5 Cadmium Column Insertion Procedure

13.5.1 Before inserting the column, pump all reagents into manifold.

13.5.2 Turn the pump off.

13.5.3 On the column, disconnect the center tubing from one of the union connectors and immediately connect to the outlet tubing of the buffer mixing coil.

13.5.4 Connect the open tubing on the column to the tee fitting where the color reagent is added. *Do not let air enter the column.*

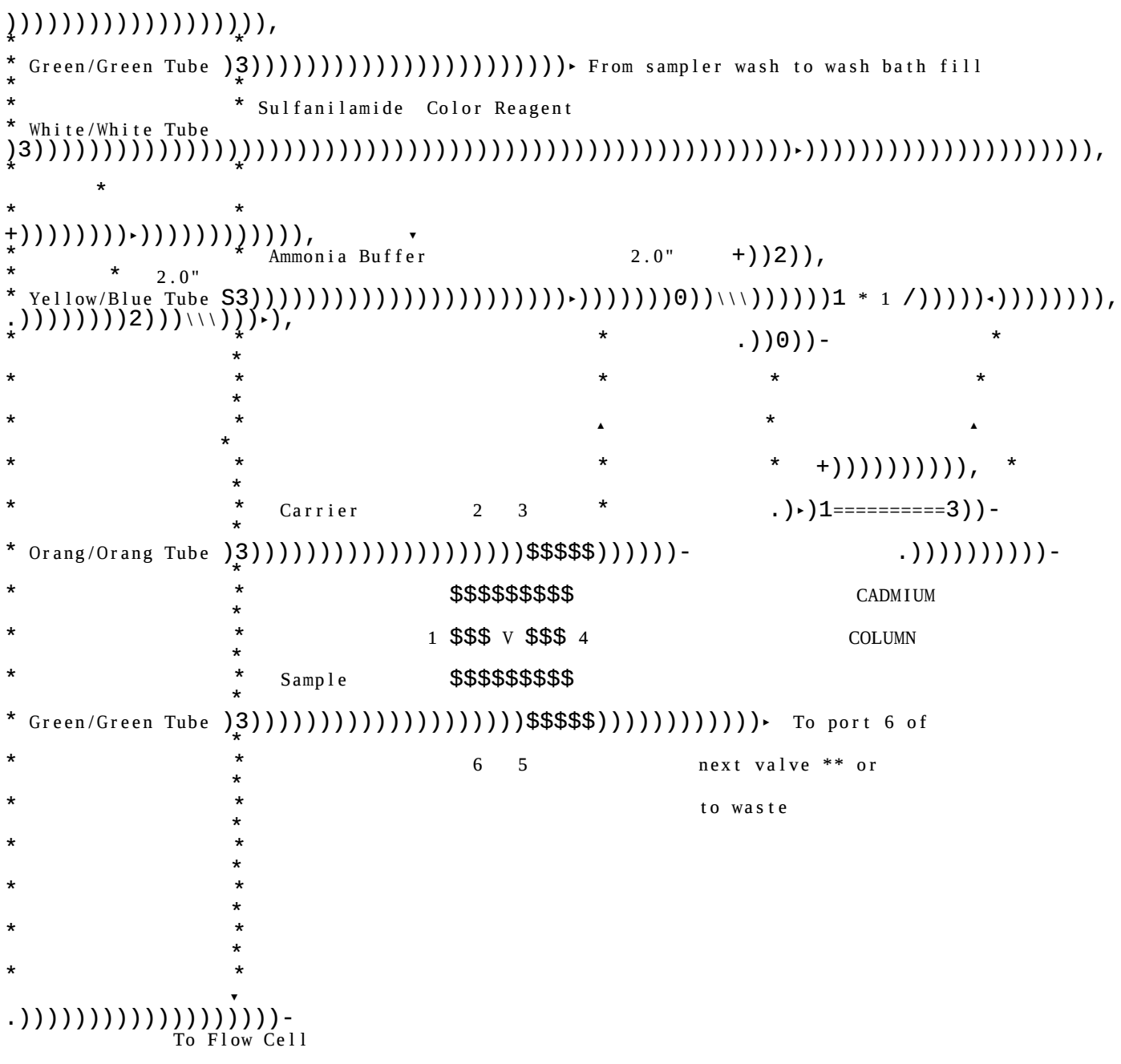
13.5.5 Return the pump to normal speed.

13.5.6 The direction of reagent flow through the column is not relevant.

14.0 References

14.1 Lachat Instruments, Method Number 10-107-04-1-C, Nitrate/Nitrite in Surface Water, Wastewater, Revision Date November 1992.

14.2 Lachat QuikChem AE Operating Manual.



Legend

2.0"
\\\ : 2.0" Mixing coil (there is 135 cm of tubing on the 2.0" coil support)

2 3
$$$
1$ V $4 : 6 Port Valve
$$$
5 6

Figure 1. Nitrate Analytical Manifold (Lake and Rain Water Analysis)

Comments

* 1. This is a 2 state switching valve used to place the cadmium column in-line with the manifold.

State One: Nitrate + Nitrite	State Two: Nitrite
Solution flow is through the cadmium column.	Solution flow by-passes the cadmium column.

1. Filter used is 520 nm.
2. Sample loop length is 25 cm.
3. All manifold tubing is 0.8 mm (0.032") ID. This relates to a flow of 5.2 µL/cm.
4. The Carrier is helium degassed DI Water.

** This will occur if more than one parameter is being run simultaneously.

NUTRIENTS SECTION QUALITY CONTROL SHEET

ANALYTE: NITRATE-NITRITE **PROGRAM:** LIMNOLOGY **DATA SET:**_____

DATE	SAMPLE		CHECK STANDARD AUDIT		BLANK AUDIT
	FROM	TO	CS-1 (LPC-1)	CS-2 (LPC-2)	REAGENT BLANK (LB)
			(0.51 to 0.69)	(0.17 to 0.23)	(-0.03 to 0.03)

COMMENTS:_____

_____

ANALYST:_____DATE:____/____/____ TEAM LEADER:_____DATE:____/____/____

NUTRIENTS SECTION QUALITY CONTROL SHEET

ANALYTE: NITRATE-NITRITE **PROGRAM:** ATMOSPHERIC WEEKLY **DATA SET:**_____

DATE	SAMPLE		CHECK STANDARD AUDIT		BLANK AUDIT		DUPLICATE AUDIT		SPIKE AUDIT $\frac{C2(V1 + V2)-C1V1}{T2V2}$ X 100%					
	FROM	TO	CS-1 (LPC-1)	CS-2 (LPC-2)	R.BLK. (LCB)	L.BLK. (LRB)	SAMP. #	DUP. (LD)	MEASURED SAMPLE CONC.	MEASURED SPIKED SAMPLE CONC.	SAMPLE VOLUME (mL)	SPIKE VOLUME (mL)	ORIG. SPIKE CONC.	%REC (LSO)
			(0.51 to 0.69)	(0.17 to 0.23)	(-0.03 to 0.03)			≤0.03	C1	C2	V1	V2	T2	88 to 112%

COMMENTS:_____

_____

ANALYST:_____DATE:____/____/____ TEAM LEADER:_____DATE:____/____/____